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REDOX STATE OF HISTORICAL GLASSES

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ABSTRACT: We studied 7 selected samples of glasses from period 4th, 13th and 18th-19th century. In 4th century was content of Fe_2O_3 about 0,4 mass %, in 13th about 0,3 mass % and in 18th about 0,03 mass %. On this bases we could conclude, that the glasses melted in the 4th century was melting for more oxidizing conditions like the glasses in 13th century. In 18th century ratio of Fe(II)/Fe(III) was degreased. We was quantified the relation between redox state and colority by the analyze of absorption spectrum of selected samples in the visible area. We can find increase of quality of technology by melting.

KEY WORDS: redox state, glass

1. INTRODUCTION

Redox state of molten glass has effect on solitary of melting process and on consequential properties of molten glass. It is effected on running of eliminates bubbles, creation of foam, corrosion of heat-resistant materials. This has effect on final colour of glass and globally on his quality. The value of redox state have been used like entering dates for mathematical modelling of distribution oxido-reduced states of component in melting space, to the modelling of behaviour ob bubbles and for identification their sources.

Redox state indicates concentration of physical bounded oxygen and ratio between various oxidative stages of elements, which are existed in glass in several oxidative stages. The clarify ingredients (e.g. Na_2SO_4, As_2O_3, Sb_2O_3, CeO_2), colouring agents (e.g. Fe_2O_3, Cr_2O_3, CoO), are addition or bring into the glass like contaminations (Fe_2O_3). These components have induced the change of oxido-reduced equilibrium of elements, which are exist in several oxidative stages and they sensitive respond on the conditions of melting too and they are shared on final colour tone „colourless" glasses.

Oxygen and elements in several oxidative stages are in equilibrium each other. This oxido-reduced equilibrium we can to convey with universal equation:

$$A^{(n-z)+} + \frac{z}{4}O_2 \xleftrightarrow{K_A(T)} A^{n+} + \frac{z}{2}O^{II-}$$

where A^n is element in oxidize state, A^{n-z} is element in reduce state; z is number of transferred electron of k or form ion A, K_A is constant of equilibrium reaction.

1.1 Oxygen is bounded physical and chemical in molten glass

Chemical bounded is oxygen on three forms: bridge oxygen (bonds Si – O – Si) indicated like O^0, non-bridge oxygen (Si – O –) indicated like O^- and of the so-called free oxygen ion indicated like O^{2-}, which is bringed into by released gasses. The equilibrium exit between chemical and physical bounded oxygen too. Physical bounded oxygen -O_2- we can introduced like soluble gas oxygen in molten glass.

Equilibrium between ions of iron v molten glass we can convey by equation:

$$2O^{2-} + 4Fe^{3+} = 4Fe^{2+} + O_2$$

If we took out the melting to the atmosphere which contains oxygen, come into being of ratio between ions of iron (II) and ions of iron (III). Redox equilibrium between of s of iron (II) and ions of iron (III) induce other factors too, especially partial pressure of oxygen, temperature, time and conditions of melting, concentration of ions of element, which are occurred in multiple oxidative stages as well as chemical composition of melting

1.2 Effect of partial pressure of oxygen

That relation shows suitable style relation between redox equilibrium of ions of element, which are occurred in multiple oxidative stages to partial pressure of oxygen:

$$-\log pO_2 = \left(\frac{4}{z}\right)\log\left(\frac{[A^{n-z}]}{[A^n]}\right) + A$$

If increases partial pressure of oxygen, than change redox equilibrium in melting of glass and this supports advanced creation of element in oxidize stage – iron (III) and up side down. [1 - 4]

1.3 Effect of temperature and time of melting

We can convey the temperature change dependent on redox equilibrium in melting at persistent partial pressure of oxygen with that relation:

$$\log\left(\frac{[A^{n-z}]}{[A^n]}\right) = \frac{\Delta H^\theta}{2{,}303RT} + B,$$

When we increase temperature of melting, thus we achieve more reducer conditions, we change redox equilibrium and support bigger creation of reduce ions of elements.

1.4 Effect of charging materials and composition of glass

If in the melting we can find two or more elements in multiple oxidative stages, there can come into being within relative reaction:

$$A^n + B^m \xleftrightarrow{K_{AB}} A^{n-z} + B^{m+z}$$

In relative reaction within occurs change of oxidize stages. Redox equilibrium within ions of iron v melting of glass is influenced of type and concentration of oxides of alkaline metals, metal of alkaline earths and aluminium. We can simply tell, that increased contents of oxides of alkaline metals, smaller size of alkali cation, decreased contents of Al_2O_3, CaO and MgO supports more oxidize stage of element – creation of ions of iron (III).

2. EXPERIMENTAL

We observed 7 selected samples of glasses from localities Zoborský Kláštor, hrad Markušovce a Tesárske Mlyňany. Sample of glasses was subjected microscopic and chemical analyze.

Tab. 1: Main archeologically informations about samples

Sample	Place of sentence	Depth [cm]	Century	*Description of samples*
S1, S5, S9, S11	Zoborský Kláštor	-	16th	*Shards colourless clear panelled glass*
B2	Hrad Markušovce	0 - 40	18-19th	*Bottom of angular glass with a bit of sheet, white colourless clear glass*
B12	Tesárske	40	4th	*Fragment from more closely undetermined article,*

	Mlyňany			*colourless relatively rough glass*
B13	*Tesárske Mlyňany*	*0 -13*	*4th*	*Glass from more closely undetermined article*

2.1 Decomposition of glasses

Sample of glass crushed in steel mortar and demagnetized. 0.1 g of sample weighed in teflon crucible and humidified with distilled water and added 10 ml HF. After 12 hours sample is evaporated and added 5 ml HF a 1 ml $HClO_4$. Mixture evaporated on the sand bath until escaped white gases of $HClO_4$. 5 ml HF and 1 ml $HClO_4$ was added twice and evaporated to dry. Finally we added 10 ml HNO_3 (1:1) and sample supplemented by distilled water in 100 ml volumetric flask.

Composition of glasses was determined by atomic emission (Na, K) and atomic absorption spectrometry (Ca, Mg, Pb, Al, Fe, Cu). We prepared calibration solutions in needs concentration from basic solution of element with concentration 1000 mg/l (1000 ppm). We used on the determination properly diluted solution of decomposited samples of historical glasses. SiO_2 was calculated to 100%.

Tab. 2: Composition of historical glasses in mass % expressed by oxides of individual elements

Sample	Na_2O	K_2O	CaO	MgO	Fe_2O_3	PbO	Al_2O_3	CuO	SiO_2
S1	1.01	13.36	1.62	1.00	1.55	0.0028	0.0000	0.0090	81.44
S5	0.70	11.38	10.50	1.29	0.67	0.0925	0.0588	0.0126	75.30
S9	0.48	15.89	8.33	1.27	0.51	0.0000	0.0000	0.0068	73.51
S11	0.81	19.91	2.20	1.50	0.52	0.0000	0.0000	0.0077	75.05
B2	8.25	7.68	2.21	2.98	0.02	0.0000	0.0000	0.0022	78.86
B12	16.87	0.74	2.59	0.66	0.78	0.0200	0.0004	0.0062	78.33
B13	17.72	1.05	3.57	0.64	0.73	0.0000	0.0000	0.0070	76.29

2.2 Determination of iron in samples of historical glasses

In closing plastic pot with blender we weighted about 0,1 g of sample, where granules of powder were < 0,042 mm. The sample was decomposed in flow of nitrogen by laboratory temperature with mixture 5 ml 38% HF and 5 ml 60% HCl with still mixing of solution for the duration of 30 minutes. Then we added 100 ml of hot saturated solution of H_3BO_3 for masking excess of HF and solution stirs next 10 minutes. After dissolution of salts we putted the solution in do 250 ml volumetric flask and supplements by distilled water to sign.

We pipette aliquot part form sample in the beak for determine of total iron. In the beak we added 5 ml solution of chloride hydroxylamine. The solution stays 30 minutes after mixing. Then we added 5 ml solution of 2,2′ - dipyridile and 20 ml solution of acetate ammonium and pH of solution was regulating on 5 till 7 by NH_3 or CH_3COOH. We putted solution in 100 ml volumetric flask and supplements by distilled water to sign and mixture. After 30 minutes was measured absorbance at wavelength 520 nm.

Determination of Fe(II) was reproducing with the same practice like at determination of total iron, only we didn't add solution of chloride hydroxylamine. For calculating of concentration of Fe(III) we used distension of concentrations Fe^{total} and Fe(II). Measurement of absorbance of solution we make on instrument Specord UV VIS, Carl Zeiss Jena in siliceous cuxette.

Tab. 3: Contents of Fe(II), Fe^{total}, Fe(III) and ratio of Fe(II)/Fe(III)

Sample	Fe(II) [mass %]	Fe^{total} [mass %]	Fe(III) [mass %]	Fe(II)/Fe(III)	*Century*
S1	0.102	0.198	0.096	1.063	*16.*

S5	0.120	0.280	0.160	0.748	*13.*
S9	0.135	0.309	0.174	0.775	*13.*
S11	0.129	0.307	0.179	0.719	*13.*
B2	0.010	0.029	0.020	0.490	*18.-19.*
B12	0.062	0.410	0.348	0.178	*4.*
B13	*0.096*	*0.385*	*0.290*	*0.333*	*4.*

3. DISCUSSION

A microscopic analysis provides information about infelicities of glasses like is bubbles, graxel and cords. Analyses of these infelicities we can appreciate on running of melting process. Snaps were obtained by microscope JENAVERT Carl Zeiss Jena with CCD-IRIS SONY camera.

Chemical analyses we can assume on the extraction of examined glasses, but we can estimate technological important properties, as temperature of melting, conditions of processing and other conditions. Table.2 shows the composition individual samples of historical glasses. According to obtainable values we can these 7 samples sectionalized of three groups of glasses. First group is created by glasses with marked S1, S5, S9 a S11. These glasses belong to within potash glasses, which we can see on the values of K_2O. Second group are soda glasses and here belong to glasses B12 a B13. Last one group included only one glass and it is B2, which belong within soda-potash glasses.

First group can indicate as well as ashed glass, because in 13-16th century potash was produced from ash. These glasses was melting at above temperature, what to designate, that melting process take place in longer time in more reduced system and this give rise to higher present of iron (II). Needles to say, that higher present of iron (II) subjects higher temperature, which supports creation of iron (II) and decreased of contents of alkaline. Table 3 shows the results of contents of Fe(II), Fe^{total}, Fe(III) and ratio of Fe(II) /Fe(III), where we can observe the variety between potash and soda glasses. Potash glasses involved more iron (II) like soda glasses. At soda glasses we can observe upper contents of iron (III) than at potash glasses. Especially group creates glass B2, which belong to soda-potash glasses, but in Table 3, we can shows, that glass contents small iron (II) as well as iron (III).From technological experiences results, that soda-potash glasses are melting by much heavier like soda or potash glasses. On the ground of these we can state, that bottom of angular glass with a bit of sheet from 18-19th century could be import to Slovakia form different region.

4. CONCLUSION

Glasses melting in 4th century was melting at more oxidize conditions like glasses in 13th century. Better contraction of furnaces subjects better blast. However it can be subject also fact,that raw in 4th century holded less reduce materials like in 13th century. In18th century was ratioFe(II)/Fe(III) deceased, what allocated on better technology of melting. From measurement of Fe(II)/Fe(III) can we deduced more interesting informations, but for it is needs measure more.

5. REFERENCES

[1] Kumar A., Singh, S.P., Pyare, R.: Glastechnische Berichte, 64(4): 106-108, 1991(58)

[2] Paul A.: Journal of Non-Crystaline Solids, 71: 269-278, 1985(36)

[3] Schreiber, H.D., Kozak, S.J., Fritchman, A.L.: Physics and chemistry of Glasses, 27(4): 152 - 177, 1989(18)

[4] Schreiber, H.D., Kozak, S.J., Merkel, R.C., Balasz, G.B., Jone Jr, P.W.: Journal of Non-Crystaline Solids, 84: 186-195, 1986(21)

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